



Letter to the Editor

Rate-controlling species for the sintering of $\text{LiTi}_2(\text{PO}_4)_3$

ARTICLE INFO

Keywords:

$\text{LiTi}_2(\text{PO}_4)_3$
Sintering
Point defects
Diffusion

ABSTRACT

A series of Li deficient $\text{LiTi}_2(\text{PO}_4)_3$ samples were prepared and sintered and the density was measured to determine the rate-controlling species for sintering of $\text{LiTi}_2(\text{PO}_4)_3$. It was observed that as the Li content decreased the density decreased. This result suggests that oxygen does not control sintering. A comparison of the $\text{LiTi}_2(\text{PO}_4)_3$ sintering data to sintering and diffusion data in olivine, which exhibits a similar framework structure to $\text{LiTi}_2(\text{PO}_4)_3$, suggests that P is the species which controls sintering. This suggestion was confirmed by the density results of a Li excess $\text{LiTi}_2(\text{PO}_4)_3$ sample.

Published by Elsevier B.V.

1. Introduction

Recently, there has been a renewed interest in the development of high energy Li–air batteries. One configuration involves the use of a Li anode in a non-aqueous electrolyte which is separated from an aqueous electrolyte containing the air cathode by a solid-state Li-ion conducting membrane [1]. One of the requirements for the membrane material besides high Li-ion conductivity is that it must also be chemically stable with water; as a result Li-ion conductors based on an oxygen framework are the preferred choice. In this case, there are essentially three possibilities, those based on a perovskite [2,3], garnet [4,5] or Na super ion conductor (NASICON) [6–11] structure. Of these choices, $\text{LiTi}_2(\text{PO}_4)_3$ (LTP), based on the NASICON structure, is one of the most widely investigated solid-state Li-ion conducting materials [6–11]. For LTP it has been observed that Li-ion conductivity is a strong function of density. For example, Li-ion conductivity can vary from about $2 \times 10^{-6} \text{ S cm}^{-1}$ [9] for a material with a relative density (actual density/theoretical density) around 70% to $1 \times 10^{-3} \text{ S cm}^{-1}$ for a material with a relative density close to 100% [13]. It has been suggested that high density is required to reduce grain boundary resistance [6]. In order to achieve the high densities two processing approaches are commonly used. The first approach is melting of doped-LTP followed by quenching to form a glass which is subsequently reheated to allow for the formation of a glass–ceramic [12,13]. The second approach is to use conventional sintering [6–11]. It has been observed that pure $\text{LiTi}_2(\text{PO}_4)_3$ cannot be sintered to high densities [6–11,14,15]. In order to obtain a dense material $\text{LiTi}_2(\text{PO}_4)_3$ must be doped with a trivalent impurity on the Ti site or a low melting phase added [6–11]. In both of these cases high density is achieved as a result of a second (i.e., AlPO_4) or liquid phase along the grain boundaries, which enhances sintering [6–11,14,15]. However, at present there is no data or explanation in the literature on what controls the sintering behavior of pure $\text{LiTi}_2(\text{PO}_4)_3$ and hence, why a high density material cannot be obtained after sintering.

For the case of sintering it is controlled by the concentration and mobility of the slowest species [16–19]. For the case of most oxides it is the oxygen ion which is the slowest moving species and moves via a vacancy mechanism and hence, controls sintering [16–20]. Thus, for $\text{LiTi}_2(\text{PO}_4)_3$ it is expected that oxygen vacancies will control the sintering behavior. One possible way to test this hypothesis is to alter the concentration of oxygen vacancies in $\text{LiTi}_2(\text{PO}_4)_3$ and see how this effects sintering. For example, when Li vacancies [V'_{Li}] (Kroger-Vink [16–19] notation is used) are created in $\text{LiTi}_2(\text{PO}_4)_3$, then according to the charge neutrality condition for oxidizing conditions (i.e., heat-treatment under an air atmosphere) given in Eq. (1) an increase in oxygen vacancies [$V_{\text{O}}^{\bullet\bullet}$], will result and hence, an increase in the sintering rate and a higher density will be obtained.

$$[V'_{\text{Li}}] = 2[V_{\text{O}}^{\bullet\bullet}] \quad (1)$$

It is the purpose of this note is to determine the rate-controlling species for sintering of $\text{LiTi}_2(\text{PO}_4)_3$ by varying the Li vacancy concentration (i.e., oxygen vacancy concentration) and observing its affect on density.

2. Experimental

Different Li vacancy concentration LTP samples were prepared by using Li deficient LTP. $\text{Li}_{1-x}\text{Ti}_2(\text{PO}_4)_3$ samples with $x=0.0, 0.05, 0.10, \text{ and } 0.15$ samples were chosen. The exact formulae for the lithium deficient LTP materials is of the form; $\text{Li}_{1-x}\text{Ti}_2\text{P}_3\text{O}_{12-x/2}$, which incorporates the charge compensating oxygen vacancies. However, for the rest of the paper the different sample compositions will be represented by the following formulas, $\text{LiTi}_2(\text{PO}_4)_3$, $\text{Li}_{0.95}\text{Ti}_2(\text{PO}_4)_3$, $\text{Li}_{0.90}\text{Ti}_2(\text{PO}_4)_3$ and $\text{Li}_{0.85}\text{Ti}_2(\text{PO}_4)_3$. This does not affect the results and conclusions. All samples were synthesized using a solid-state method from TiO_2 (rutile structure), Li_2CO_3 and $\text{NH}_4\text{H}_2\text{PO}_4$. The starting materials were ball milled using methanol for 6 h. The powders were ground into a fine powder and calcined at 900°C under air for 4 h in a covered alumina crucible. The resulting powder was reground and uniaxially pressed into cylindrical

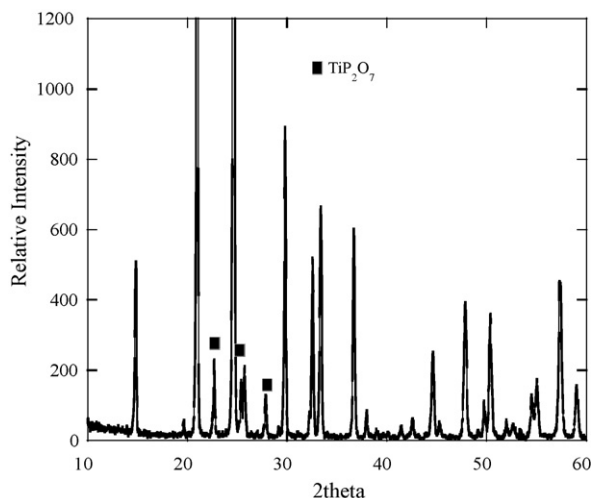
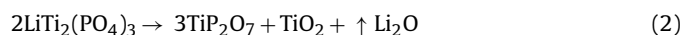


Fig. 1. X-ray diffraction pattern of $\text{LiTi}_2(\text{PO}_4)_3$ after sintering.

specimens 13 mm in diameter with a thickness between 2 and 4 mm at pressure of 200 MPa. A 5 wt.% polyvinyl alcohol binder was used. The pellets were then sintered at 950 °C for 2 h under air on platinum foil. The Li content of the samples after sintering was determined using inductively coupled plasma analysis (Galbraith Laboratories, Inc., Knoxville, TN). All samples were characterized by X-ray diffraction. Lattice constants were determined by fitting the data using Rietveld refinement [21]. The density of the sintered pellets was determined from the weight and physical dimensions.

3. Results and discussion

The $\text{LiTi}_2(\text{PO}_4)_3$, $\text{Li}_{0.95}\text{Ti}_2(\text{PO}_4)_3$, $\text{Li}_{0.90}\text{Ti}_2(\text{PO}_4)_3$ and $\text{Li}_{0.85}\text{Ti}_2(\text{PO}_4)_3$ samples were all white colored after sintering. The X-ray diffraction pattern of the $\text{LiTi}_2(\text{PO}_4)_3$ sample after sintering is shown in Fig. 1. From Fig. 1 it can be seen that there are two phases present, a majority $\text{LiTi}_2(\text{PO}_4)_3$ phase and a TiP_2O_7 second phase. Second phase TiP_2O_7 was found in all four samples. The amount of TiP_2O_7 determined using Rietveld refinement was between 4 and 6 wt.% for all four samples. TiP_2O_7 is expected according to Eq. (2) as a result of Li_2O loss during heating and has been observed in many LTP samples after calcining and/or sintering [15,22,23]. The X-ray diffraction patterns did not reveal the presence of TiO_2 .



Inductively coupled plasma analysis did confirm Li loss during heat-treatment. The actual Li content of the $\text{LiTi}_2(\text{PO}_4)_3$, $\text{Li}_{0.95}\text{Ti}_2(\text{PO}_4)_3$, $\text{Li}_{0.90}\text{Ti}_2(\text{PO}_4)_3$ and $\text{Li}_{0.85}\text{Ti}_2(\text{PO}_4)_3$ samples after heat-treatment was 0.96 ± 0.02 , 0.90 ± 0.02 , 0.85 ± 0.02 and 0.81 ± 0.02 instead of the initial values of 1.0, 0.95, 0.90 and 0.85, respectively. The fact that all the samples had the same Li loss (0.04–0.05) after heat-treatment is expected since; they were all given the exact same heat-treatment.

The X-ray diffraction pattern for the majority $\text{LiTi}_2(\text{PO}_4)_3$ phase can be indexed to a rhombohedral ($R\bar{3}c$) NASICON structure for all four samples. The lattice parameters a and c , determined from Rietveld refinement as a function of Li content (amount determined from the inductively coupled plasma analysis) are shown in Fig. 2A and B, respectively. From Fig. 2 several important points are noted. First, the lattice parameters for $\text{LiTi}_2(\text{PO}_4)_3$ are in good agreement with those in the literature [7,10,23–26]. Secondly, both the a and c lattice parameters decrease with decreasing Li content ($x \uparrow$). This result is consistent with the formation of vacancies in the Li defi-

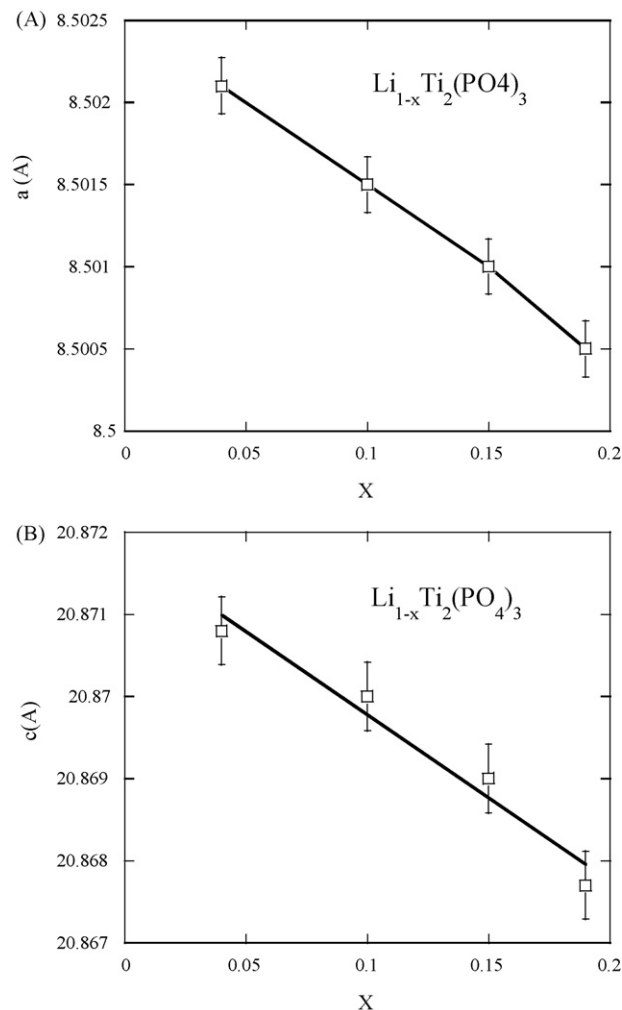


Fig. 2. Lattice parameters of $\text{Li}_{1-x}\text{Ti}_2(\text{PO}_4)_3$ as a function of x (using the Li content after sintering).

cient LTP materials. We would expect that from Eq. (1) that with decreasing Li content ($x \uparrow$) an increase in the number of oxygen vacancies and hence, an increase in density.

Fig. 3 is a plot of relative density versus Li content (amount determined from the inductively coupled plasma analysis) for the $\text{LiTi}_2(\text{PO}_4)_3$, $\text{Li}_{0.95}\text{Ti}_2(\text{PO}_4)_3$, $\text{Li}_{0.90}\text{Ti}_2(\text{PO}_4)_3$ and $\text{Li}_{0.85}\text{Ti}_2(\text{PO}_4)_3$ samples. The relative density is the actual density obtained from the weight and physical dimensions divided by the theoretical density of the sample, $\rho_{\text{theo sample}}$, given in the following equation:

$$\rho_{\text{theo sample}} = \rho_{\text{theo LTP}} f_{\text{LTP}} + \rho_{\text{theo TiP}_2\text{O}_7} f_{\text{TiP}_2\text{O}_7} \quad (3)$$

where $\rho_{\text{theo LTP}}$ is the theoretical density of LTP (changing from $\text{LiTi}_2(\text{PO}_4)_3$, to $\text{Li}_{0.85}\text{Ti}_2(\text{PO}_4)_3$ has <1% difference in density, hence the density value for LTP from the JPDF X-ray PDF file, #00-35-754 was used, 2.948 g cm^{-3}), $\rho_{\text{theo TiP}_2\text{O}_7}$ is the theoretical density of TiP_2O_7 (3.014 g cm^{-3} , JPDF X-ray PDF file #00-038-1468), f_{LTP} is the fraction of LTP and $f_{\text{TiP}_2\text{O}_7}$ is the fraction of TiP_2O_7 . For the four different LTP samples since, the amount of TiP_2O_7 was nearly the same in all four samples (4–6 wt.%), $f_{\text{TiP}_2\text{O}_7} = 5 \text{ wt.}\%$ and $f_{\text{LTP}} = 95 \text{ wt.}\%$ was used in calculating $\rho_{\text{theo sample}}$. Inserting these values into Eq. (3) results in 95% of the sample density coming from the LTP phase thus, any trend in the density data with Li content must be due to the behavior of the LTP phase. From Fig. 3 several important points are noted. First, the relative density of $\text{LiTi}_2(\text{PO}_4)_3$ is 69%. This value

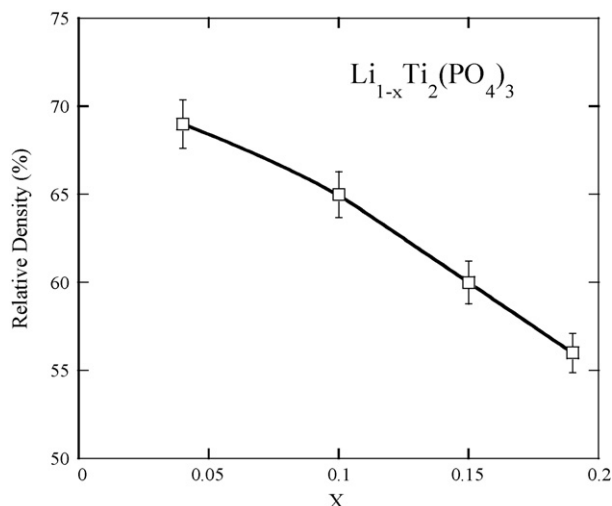


Fig. 3. Relative density of $\text{Li}_{1-x}\text{Ti}_2(\text{PO}_4)_3$ as a function of x (using the Li content after sintering).

is in good agreement with the value of 66% for $\text{LiTi}_2(\text{PO}_4)_3$ sintered at almost the same temperature (900 °C) for the same time (2 h) recorded by Aono et al. [8]. It is also in agreement with the value of 69% observed by Yamamoto et al. [27] for $\text{LiGe}_2(\text{PO}_4)_3$ sintered at 900 °C for 2 h. Secondly, as the Li content (x) increases the relative density decreases. This result reveals as the number of Li vacancies increases and hence, the number of oxygen vacancies increases a decrease in density is exhibited. This is opposite of what is expected if oxygen vacancies control sintering. For the case of sintering controlled by oxygen vacancies an increase in density should be observed as the number of oxygen vacancies increases. This result suggests oxygen vacancies are not the rate-controlling species. This observation is not unreasonable when the LTP sintering results are compared to sintering and diffusion data for olivine materials. The basic LTP structure consists of a three-dimensional framework of TiO_6 octahedra interconnected with PO_4 tetrahedra [6,25,26]. The basic olivine structure can be characterized by MO_6 octahedra (where M is a metal) interconnected with SiO_4 tetrahedra [16–18]. Since, both LTP and olivine have a similar structure, the sintering and diffusion data for olivine can be used as a guide to determine the rate-controlling species for the sintering of LTP. For the case of olivine, diffusion and sintering studies have revealed that Si not oxygen is the slower moving species and hence, controls sintering [28–30]. Based upon this, it is highly likely that P is the species that controls the sintering rate of LTP. If this is true and assuming that the ionic defects in LTP form Schottky defects (vacancies) rather than Frenkel defects (interstitials), then the Schottky defect equilibria reaction for $\text{LiTi}_2(\text{PO}_4)_3$ is given in the following equation:

$$[V_{\text{Li}}] [V_{\text{Ti}}]^{2} [V_{\text{P}}]^{3} [V_{\text{O}}]^{12} = K_{\text{S}} \quad (4)$$

where $[V_{\text{Ti}}]$ is a titanium vacancy, $[V_{\text{P}}]$ is a phosphorous vacancy and K_{S} is the Schottky equilibrium constant. From Eq. (4) it is observed that the product of the Li, Ti, P and O vacancy concentrations is fixed at a given temperature. Thus, if one concentration is changed the others must vary to keep this product constant. For our case we have increased both the Li and O vacancy concentrations as LTP becomes more Li deficient, as a consequence according to Eq. (4) the Ti and P vacancy concentrations must decrease. As a result of the decreased P vacancy concentration, assuming that P is rate controlling, we will have lower sintering rate and hence, a lower density will be achieved. The results shown in Fig. 3 reveal a lower density is

achieved as the Li and O vacancy concentrations increase, in agreement with the suggestion that P is the rate-controlling species for the sintering of LTP.

To confirm this suggestion, a LTP sample with excess Li was prepared. A Li excess $\text{Li}_{1+x}\text{Ti}_2(\text{PO}_4)_3$ sample with a starting $x = 0.10$ was prepared and sintered under the same conditions as that for the $\text{LiTi}_2(\text{PO}_4)_3$, $\text{Li}_{0.95}\text{Ti}_2(\text{PO}_4)_3$, $\text{Li}_{0.90}\text{Ti}_2(\text{PO}_4)_3$ and $\text{Li}_{0.85}\text{Ti}_2(\text{PO}_4)_3$ samples. X-ray diffraction of the $\text{Li}_{1.1}\text{Ti}_2(\text{PO}_4)_3$ sample also revealed not only the majority $\text{LiTi}_2(\text{PO}_4)_3$ phase but also a TiP_2O_7 second phase, just like for the case of the Li deficient LTP samples. Rietveld refinement revealed the amount of TiP_2O_7 second phase was 4 wt.% in the $\text{Li}_{1.1}\text{Ti}_2(\text{PO}_4)_3$ sample, an amount similar to that observed for the Li deficient LTP samples. The final Li content of the $\text{Li}_{1.1}\text{Ti}_2(\text{PO}_4)_3$ sample was not analyzed. However, based on the inductively coupled plasma results for Li deficient LTP samples which had a Li loss (0.04–0.05) after heat-treatment it is expected that actual Li content of the $\text{Li}_{1.1}\text{Ti}_2(\text{PO}_4)_3$ sample is about 1.05 instead of 1.10, which still makes this sample Li excess.

For the case of Li excess LTP the charge neutrality condition is given by the following equation:

$$[L_i] = 4[V_{\text{Ti}}] + 5[V_{\text{P}}] \quad (5)$$

where $[L_i]$ is the concentration of extra Li on interstitial sites. At present it is not possible to determine if one type of vacancy, Ti or P is dominant. However, from Eq. (5) it can be observed that the extra Li results in an increase in the number of Ti and P vacancies in the Li excess LTP compared to $\text{LiTi}_2(\text{PO}_4)_3$. Assuming P is the rate-controlling species for sintering then, a higher density is expected for the Li excess LTP compared to $\text{LiTi}_2(\text{PO}_4)_3$. The $\text{Li}_{1.1}\text{Ti}_2(\text{PO}_4)_3$ sample had a relative density of 74% compared 69% for $\text{LiTi}_2(\text{PO}_4)_3$. This result adds further confirmation that P is the rate-controlling species for sintering of $\text{LiTi}_2(\text{PO}_4)_3$. The results of this study suggest that in order to obtain highly dense $\text{LiTi}_2(\text{PO}_4)_3$ without the addition of secondary phases along grain boundaries through conventional sintering point defects which increase the concentration of P vacancies, such as adding excess Li are needed.

4. Conclusions

A series of Li deficient LTP samples, $\text{LiTi}_2(\text{PO}_4)_3$, $\text{Li}_{0.95}\text{Ti}_2(\text{PO}_4)_3$, $\text{Li}_{0.90}\text{Ti}_2(\text{PO}_4)_3$ and $\text{Li}_{0.85}\text{Ti}_2(\text{PO}_4)_3$ were prepared and sintered and the density was measured to determine the rate-controlling species for sintering of $\text{LiTi}_2(\text{PO}_4)_3$. It was observed that as the Li content (i.e., the number of Li vacancies and oxygen vacancies) decreased the density decreased. This trend is opposite of what is expected if oxygen vacancies control sintering. A comparison of the LTP sintering results to diffusion and sintering data in olivine, which exhibits a similar structure to LTP, suggests that P is the species which controls sintering of $\text{LiTi}_2(\text{PO}_4)_3$. This suggestion was confirmed by the higher density of a Li excess LTP sample compared to $\text{LiTi}_2(\text{PO}_4)_3$. In order to obtain highly dense $\text{LiTi}_2(\text{PO}_4)_3$, without the addition of secondary phases along grain boundaries, using conventional sintering, point defects which increase the concentration of P vacancies (i.e., for example, adding excess Li) are needed.

Acknowledgement

The authors would like to acknowledge support of the U.S. Army Research Laboratory.

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31 March 2008

Available online 29 April 2008